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METHOD FOR MANUFACTURING POLYMERIZED "NONMETALLOCENE" OLEFIN
POLYMERIZATION CATALYST

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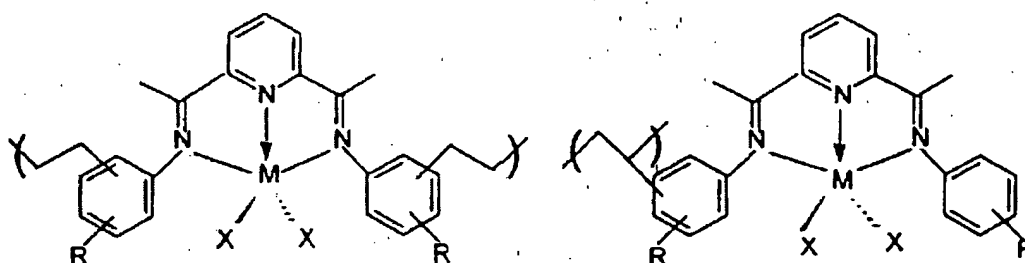
Abstract

The present invention pertains to the manufacture of a polymerized late transition metal "nonmetallocene" olefin polymerization catalyst. The catalyst consists of two components, that is components A and B. The chemical formula of component A is $[P(S\text{-}co\text{-}Cat)]$, wherein P represents a copolymer, S represents polystyrene, co represents copolymerization, and Cat represents a "nonmetallocene" catalyst. Cat is a coordination compound formed from a tridentate

nitrogen neutral ligand and a metal M. Component B is methylaluminoxane or boron pentachlorobenzene. These two types of catalysts have a relatively high catalytic activity when used for ethylene polymerization. The polymerization product contains no inorganic ash.

Claims

1. A method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts characterized by the following facts: the catalysts consist of two components, that is components A and B; the chemical formula of component A is $[P(S-co-Cat)]$, wherein P represents a copolymer, S represents polystyrene, co represents copolymerization, and Cat represents a "nonmetallocene" catalyst; the structure is as follows:

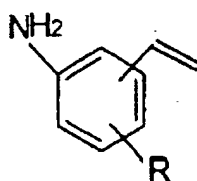


wherein, $M = Fe, Co$; $X = Cl, Br$; R is any type selected from H, Me, i-Pr, t-Bu; Cat is a coordination compound formed from a tridentate nitrogen neutral ligand and metal M; component B is methylaluminoxane or boron pentachlorobenzene;

the catalyst is manufactured as follows:

1) preparation of an alkylene arylamine

the structure is as follows:



under oxygen-free and anhydrous conditions, with 50-70 mL of tetrahydrofuran used as the solvent, under cooling of ice water, 51-74 mmol of methyltriphenylphosphorous bromide is added to react with 51-78 mmol of n-butyllithium; after 30-60 min, 50-74 mmol of a nitroarylaldehyde are added, and the reaction is carried out for 12-18 h; the obtained mixed solution is washed with brine, followed by extraction using trichloromethane; after drying with anhydrous sodium sulfate, the extract is concentrated in vacuo; the remaining solution is passed through a silica gel column for separation with 1:1 toluene/hexane used as the rinsing agent; as a result, a nitroarylethylene is obtained at a yield of 72-89%; then, the product is reduced through an iron - acetic acid - alcohol system to obtain an alkylene arylamine at a yield of 56-60%;

2) preparation of symmetric tridentate ligand containing two alkylene groups

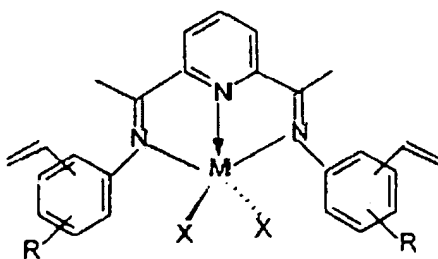
with 20-30 mL of methanol used as the solvent, 1-2 mL of glacial acetic acid, 0.94-1.5 mL of an alkylene arylamine, and 3.05-4.9 mmol of 2,6-diacetylpyridine are heated to slightly boiling under the protection of argon, followed by 4 h of reflux and concentration in vacuo; then, the reaction product is added to 30 mL of deionized water and extracted using ethyl ether; the extract is dried with anhydrous sodium sulfate and concentrated; the system is cooled for crystallization to obtain a diimino ligand as yellow crystals at a yield of 80-85%;

3) preparation of asymmetric tridentate ligand containing one alkylene group

with 20-30 mL of anhydrous alcohol used as the solvent and 0.5-1 mL of glacial acetic acid used as the catalyst, 0.8-1.5 mL of an alkylene arylamine is reacted with 6.1-11.4 mmol of 2,6-diacetylpyridine under stirring at room temperature for 3-4 days; the solution is light yellow in color; after the solvent is removed, 30-40 mL of deionized water are added; a yellow precipitate appears and is filtered; the precipitate is recrystallized using n-hexane to obtain a monoimino compound; 3.8-5.0 mmol of the obtained monoimino compound, 8.3-10.9 mmol of an arylamine, and 1-2 mL of glacial acetic acid are added to 20-30 mL of methanol, followed by 2-3 h of reflux performed under the protection of argon; after the solvent is removed, the system is cooled for crystallization, giving an asymmetric diimino ligand at a yield of 53-65%;

4) preparation of symmetric late transition metal catalyst containing two alkylene groups

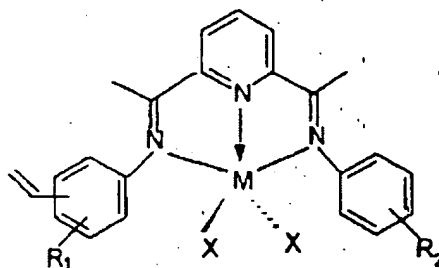
the structure is as follows:



the catalyst is prepared under oxygen-free and anhydrous conditions and under the protection of highly pure argon; with 30-40 mL of tetrahydrofuran used as the solvent, the symmetric diimino ligand and iron dichloride tetrahydrate or anhydrous cobalt dichloride are added at an amount ratio of 1:1:1 and stirred at room temperature for 1-2 h, followed by concentration in vacuo; n-hexane is added to precipitate a solid powder, which is washed 3-5 times with n-hexane, followed by drying in vacuo; the yield is 95-98%;

5) preparation of asymmetric late transition metal catalyst containing one alkylene group

the structure is as follows:



the catalyst is prepared under oxygen-free and anhydrous conditions and under the protection of highly pure argon; with 30-40 mL of tetrahydrofuran used as the solvent, the asymmetric ligand and iron dichloride tetrahydrate or anhydrous cobalt dichloride are added at an amount ratio of 1.05:1 and stirred at room temperature for 1.5-3 h, followed by concentration in vacuo; n-hexane is added to precipitate a solid powder, which is washed 3-5 times with n-hexane, followed by drying in vacuo; the yield is 92-96%;

6) preparation of polymerized "nonmetallocene" catalyst

under oxygen-free and anhydrous conditions, 2-10 mmol of the alkylene-containing "nonmetallocene" catalyst, 5-10 mL of styrene and 0.05-0.14 g of azodiisobutyronitrile are added sequentially to boiling dimethylamide, where they are mixed homogenously; then, copolymerization is carried out in an 80°C water bath for 12-15 h; after that, the dimethylamide is removed under heat to obtain a gel-like substance, which is dissolved using 30 mL of toluene, followed by centrifugation; the supernatant is treated with n-hexane used as a precipitating agent to obtain a solid powder, which is washed with n-hexane three times, followed by drying; ethylene polymerization is carried out under oxygen-free and anhydrous conditions; 100 mL of toluene or hexane, methylaluminoxane, polymerized catalyst Al/M=500-2500 and ethylene are added sequentially to the reaction system; the reaction is carried out at 25-50°C for 1 h; a methanol solution containing 1% hydrochloric acid is used to end the reaction; the obtained product is filtered and washed with methanol three times, followed by drying in vacuo at 40°C for 24 h.

2. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact that the symmetric diimino ligand and iron dichloride tetrahydrate are added at a ratio of 1.1:1.

3. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact that the the symmetric diimino ligand and anhydrous cobalt dichloride are added at a ratio of 1.1:1.

4. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact the asymmetric diimino ligand and iron dichloride tetrahydrate are added at a ratio of 1.05:1.

5. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact that the asymmetric diimino ligand and anhydrous cobalt dichloride are added at a ratio of 1.05:1.

6. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact that the aforementioned ethylene polymerization is carried out under oxygen-free and anhydrous conditions, and 100 mL of toluene are added to the reaction system.

7. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact that the aforementioned ethylene polymerization is carried out under oxygen-free and anhydrous conditions, and 100 mL of hexane are added to the reaction system.

8. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact that the aforementioned ethylene polymerization is carried out under oxygen-free and anhydrous conditions and methylaluminoxane and polymerized catalyst Al/M=500-2500 are added to the reaction system.

9. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact that the aforementioned ethylene polymerization is carried out under oxygen-free and anhydrous conditions, and ethylene is added to the reaction system.

Specification

The present invention pertains to a method for manufacturing polymerized "nonmetallocene" late transition metal olefin polymerization catalysts.

Polyolefin is a prominent material in the modern polymer materials industry. Millions of tons of polyolefin products are manufactured annually. These products improve the quality of life of people. Under the effect of catalysts, olefins are polymerized to generate polymers. Polyolefin products with special structures and properties can be obtained by varying the structure of the catalysts. Therefore, the catalyst is the key to the polyolefin industry. In recent years, a series of new olefin polymerization catalysts with one active center have been discovered that are based on metallocene catalysts. This series of catalysts can be roughly classified into two types: a. nonmetallocene compounds and non-group IVB transition metal compounds; b. polyimino compounds of late transition metals, such as nickel, palladium, iron, cobalt, etc. Since this series of catalysts were discovered after the metallocene catalysts, they are generally called "nonmetallocene" olefin polymerization catalysts.

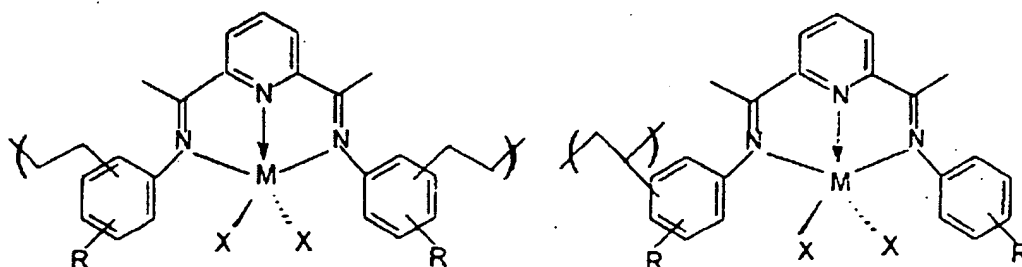
In 1998, Brookhart, et al. and the Du Pont Co. (J. Am. Chem. Soc. 120. 4049 (1998), WO98/30612, WO98/27214) and Gibson, et al. and the BP Co. (Chem. Commun. 849. 1998,

WO99/12981) reported that polyimino compounds of iron and cobalt are able to catalyze olefin polymerization in the presence of an auxiliary catalyst MMAO and show very high activity. This discovery opened a new field of research of "nonmetallocene" olefin polymerization catalysts. When the polyiminio compound of iron or cobalt is used to catalyze ethylene polymerization to generate linear high-density polyethylene, the molecular weight of the polymer is easily affected by substituents, the central metal atom, and the concentration of the active points. The Brookhart group and the Gibson group studied the influences of the substituents at positions 2, 4, 6 in arylamines on the structure and catalytic property of the catalyst. The substituents included methyl, isopropyl, and tert-butyl groups. From the research it was found that larger substituents at positions 2, 6 tend to generate polyethylene with a high molecular weight. So far, there has been no report on carrying late transition metal "nonmetallocene" catalysts on solid carriers. A solid carrier is significant in terms of making this type of catalyst suitable for industrial apparatuses.

The purpose of the present invention is to provide a method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts. This method uses an alkylene containing a polyimino compound of iron or cobalt and styrene to couple a "nonmetallocene" catalyst to a polymer chain via the σ chain under the effect of an initiator to form a polymerized "nonmetallocene" olefin polymerization catalyst.

The polymerized "nonmetallocene" catalyst also has very high catalytic activity in olefin polymerization. In addition, when the "nonmetallocene" catalyst is polymerized, it becomes very easy to control the composition and distribution of the catalyst on the polymer chain. The catalytic effect of the active center can be fully displayed by adjusting the distribution of the catalyst on the polymer chain. Also, the polymer obtained by using the polymerized "nonmetallocene" catalyst to catalyze the olefin polymerization contains no ash component.

The catalyst of the present invention consists of two components, that is components A and B. The chemical formula of component A is $[P(S\text{-co-Cat})]$, wherein P represents a copolymer, S represents polystyrene, co represents copolymerization, and Cat represents a "nonmetallocene" catalyst. The structure is as follows:

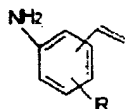


wherein, M=Fe, Co; X=Cl, Br; R is any type selected from H, Me, I-Pr, t-Bu. Cat is a coordination compound formed from a tridentate nitrogen neutral ligand and a metal M. Through copolymerization with styrene, the alkylene groups at the ortho, meta, para positions in the amine can couple the catalyst to a polymer chain via the σ chain to obtain the polymerized "nonmetallocene" olefin polymerization catalyst. Component B is methylaluminoxane or boron pentachlorobenzene.

The catalyst is manufactured as follows:

1) Preparation of alkylene arylamine

The structure is as follows:



Under oxygen-free and anhydrous conditions, with 50-70 mL of tetrahydrofuran used as the solvent, under cooling of ice water, 51-74 mmol of methyltriphenylphosphorous bromide is added to react with 51-78 mmol of n-butyllithium. After 30-60 min, 50-74 mmol of nitroarylaldehyde is added, and the reaction is carried out for 12-18 h. The obtained mixed solution is washed with brine, followed by extraction using trichloromethane. After drying with anhydrous sodium sulfate, the extract is concentrated in vacuo; the remaining solution is passed through a silica gel column for separation with 1:1 toluene/hexane used as the rinsing agent. As a result, a nitroarylethylene is obtained at a yield of 72-89%. Then, the product is reduced through an iron - acetic acid - alcohol system to obtain an alkylene arylamine at a yield of 56-60%.

2) Preparation of symmetric tridentate ligand containing two alkylene groups

With 20-30 mL of methanol used as the solvent, 1-2 mL of glacial acetic acid, 0.94-1.5 mL of an alkylene arylamine, and 3.05-4.9 mmol of 2,6-diacetylpyridine are heated to slightly boiling under the protection of argon, followed by 4 h of reflux and concentration in vacuo. Then, the reaction product is added to 30 mL of deionized water and extracted using ethyl ether. The extract is dried with anhydrous sodium sulfate and concentrated. The system is cooled for crystallization to obtain a diimino ligand as yellow crystals at a yield of 80-85%.

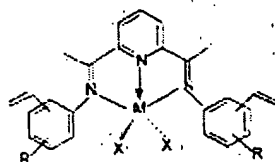
3) Preparation of asymmetric tridentate ligand containing one alkylene group

With 20-30 mL of anhydrous alcohol used as the solvent and 0.5-1 mL of glacial acetic acid used as the catalyst, 0.8-1.5 mL of an alkylene arylamine is reacted with 6.1-11.4 mmol of 2,6-diacetylpyridine under stirring at room temperature for 3-4 days. The solution is light yellow in color. After the solvent is removed, 30-40 mL of deionized water are added. A yellow precipitate appears and is filtered. The precipitate is recrystallized using n-hexane to obtain a

monoimino compound. 3.8-5.0 mmol of the obtained monoimino compound, 8.3-10.9 mmol of an arylamine, and 1-2 mL of glacial acetic acid are added to 20-30 mL of methanol, followed by 2-3 h of reflux performed under the protection of argon. After the solvent is removed, the system is cooled for crystallization, giving an asymmetric diimino ligand at a yield of 53-65%.

4) Preparation of symmetric late transition metal catalyst containing two alkylene groups

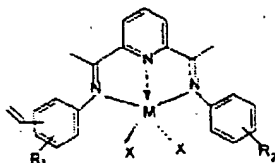
The structure is as follows:



The catalyst is prepared under oxygen-free and anhydrous conditions and under protection of highly pure argon. With 30-40 mL of tetrahydrofuran used as the solvent, the symmetric diimino ligand and iron dichloride tetrahydrate or anhydrous cobalt dichloride are added in an amount ratio of 1.1:1 and stirred at room temperature for 1-2 h, followed by concentration in vacuo; n-hexane is added to precipitate a solid powder, which is washed 3-5 times with n-hexane, followed by drying in vacuo. The yield is 95-98%.

5) Preparation of asymmetric late transition metal catalyst containing one alkylene group

The structure is as follows:



The catalyst is prepared under oxygen-free and anhydrous conditions and under protection of highly pure argon. With 30-40 mL of tetrahydrofuran used as the solvent, the asymmetric ligand and iron dichloride tetrahydrate or anhydrous cobalt dichloride are added in an amount ratio of 1.05:1 and stirred at room temperature for 1.5-3 h, followed by concentration in vacuo; n-hexane is added to precipitate a solid powder, which is washed 3-5 times with n-hexane, followed by drying in vacuo. The yield is 92-96%.

6) Preparation of polymerized "nonmetallocene" catalyst

Under oxygen-free and anhydrous conditions, 2-10 mmol of the alkylene-containing "nonmetallocene" catalyst, 5-10 mL of styrene, 0.05-0.14 g of azodiisobutyronitrile are added sequentially to boiling dimethylamide, where they are mixed homogenously. Then, copolymerization is carried out in an 80°C water bath for 12-15 h. After that, the dimethylamide

is removed as much as possible under heating to obtain a gel-like substance, which is dissolved using 30 mL of toluene, followed by centrifugation. The supernatant is treated with n-hexane used as a precipitating agent to obtain a solid powder, which is washed with n-hexane three times, followed by drying.

Ethylene polymerization is carried out under oxygen-free and anhydrous conditions. 100 mL of toluene or hexane, methylaluminoxane, polymerized catalyst Al/M=500-2500 and ethylene are added sequentially to the reaction system. The reaction is carried out at 25-50°C for 1 h. A methanol solution containing 1% hydrochloric acid is used to end the reaction. The obtained product is filtered and washed with methanol three times, followed by drying in vacuo at 40°C for 24 h.

The application examples of the present invention are as follows.

Application Example 1: Preparation of alkylene arylamine

In an argon atmosphere, 51 mmol of methyltriphenylphosphorous bromide were dissolved in 50 mL of dry tetrahydrofuran. Under cooling of ice water, 32 mL of 1.6M n-butyllithium are added to the solution. After 30 min, 100 mL of a tetrahydrofuran solution containing 50 mmol of o-nitrobenzaldehyde were added, and the reaction was carried out for 12 h. The obtained mixed solution was washed with brine, followed by extraction using trichloromethane. After drying with anhydrous sodium sulfate, the extract was concentrated in vacuo. The remaining solution was passed through a silica gel column for separation with toluene/hexane 1:1 used as the rinsing agent. As a result, 6.63 g of a yellow liquid, o-nitrostyrene, was obtained at a yield of 89.0%. 45 mmol of the obtained n-nitrostyrene were dissolved in a mixed solution consisting of 50 mL of glacial acetic acid and 50 mL of anhydrous alcohol, followed by adding 0.178 mmol of iron powder. The mixed solution was refluxed under the protection of argon for 1h. After the system was cooled to room temperature, the reaction product was added to 350 mL of water and neutralized with solid sodium carbonate. The condensed solution was extracted with ether, followed by concentration in vacuo. A small amount of benzenediol was added to the remaining solution, followed by distillation under reduced pressure, giving 3.2 g of a colorless liquid, o-aminostyrene, at a yield of 60.0%.

Application Example 2: Preparation of alkylene arylamine

The process was carried out in the same way as described in Application Example 1 except that m-nitrobenzaldehyde was used in an amount of 50 mmol, and 2.17 g of m-aminostyrene were obtained at a yield of 41.5%.

Application Example 3: Preparation of alkylene arylamine

The process was carried out in the same way as described in Application Example 1 except that p-nitrobenzaldehyde was used in an amount of 50 mmol, and 3.02 g of p-aminostyrene were obtained at a yield of 50.7%.

Application Example 4: Preparation of alkylene arylamine

In an argon atmosphere, 74 mmol of methyltriphenylphosphorous bromide was dissolved in 70 mL of dry tetrahydrofuran. Under cooling of ice water, 48.8 mL of 1.6M n-butyllithium are added to the solution. After 50 min, 100 mL of a tetrahydrofuran solution containing 74 mmol of 3-nitro-4-methylbenzaldehyde were added, and the reaction was carried out for 16 h under stirring. The obtained mixed solution was washed with brine, followed by extraction using trichloromethane. After drying with anhydrous sodium sulfate, the extract was concentrated in vacuo. The remaining solution was passed through a silica gel column for separation with 1:1 toluene/hexane used as the rinsing agent. As a result, 8.68 g of a yellow liquid, 3-nitro-4-methylstyrene, were obtained at a yield of 72.0%. 45 mmol of the obtained n-nitrostyrene [sic] were dissolved in a mixed solution consisting of 50 mL of glacial acetic acid and 50 mL of anhydrous alcohol, followed by adding 0.178 mmol of iron powder. The mixed solution was refluxed under the protection of argon for 1 h. After the system was cooled to room temperature, the reaction product was added to 350 mL of water and neutralized with solid sodium carbonate. The condensed solution was extracted with ether, followed by concentration in vacuo. A small amount of benzenediol was added to the remaining solution, followed by distillation under reduced pressure, giving 3.41 g of a colorless liquid, 3-amino-4-methylstyrene, at a yield of 57%.

Application Example 5: Preparation of alkylene arylamine

In an argon atmosphere, 60 mmol of methyltriphenylphosphorous bromide was dissolved in 60 mL of dry tetrahydrofuran. Under cooling of ice water, 37.5 mL of 1.6M n-butyllithium are added to the solution. After 60 min, 100 mL of a tetrahydrofuran solution containing 60 mmol of 3-isopropyl-4-nitrobenzaldehyde was added, and the reaction was carried out for 18 h under stirring. The obtained mixed solution was washed with brine, followed by extraction using trichloromethane. After drying with anhydrous sodium sulfate, the extract was concentrated in vacuo. The remaining solution was passed through a silica gel column for separation with 1:1 toluene/hexane used as the rinsing agent. As a result, 9.11 g of a yellow liquid, 3-isopropyl-4-nitrostyrene, was obtained at a yield of 79.5%. 45 mmol of the obtained n-nitrostyrene [sic] were dissolved in a mixed solution consisting of 50 mL of glacial acetic acid and 50 mL of anhydrous alcohol, followed by adding 0.178 mmol of iron powder. The mixed

solution was refluxed under the protection of argon for 1 h. After the system was cooled to room temperature, the reaction product was added to 350 mL of water and neutralized with solid sodium carbonate. The condensed solution was extracted with ether, followed by concentration in vacuo. A small amount of benzenediol was added to the remaining solution, followed by distillation under reduced pressure, giving 4.06 g of a colorless liquid, 3-isopropyl-4-nitrostyrene, at a yield of 56.0%.

Application Example 6: Preparation of asymmetric tridentate ligand containing one alkylene group

With 20 mL of anhydrous alcohol used as the solvent and 0.5 mL of glacial acetic acid used as the catalyst, 0.8 mL of o-aminostyrene was reacted with 6.1 mmol of 2,6-diacetylpyridine under stirring at room temperature for 3 days. The solution was light yellow in color. After most of the solvent was removed, 30 mL of deionized water were added. A yellow precipitate appeared and was filtered. The precipitate was recrystallized using n-hexane to obtain a monoimino compound of columnar crystals. 3.8 mmol of the obtained monoimino compound, 8.3 mmol of 2,6-dimethylaniline, and 1 mL of glacial acetic acid were added to 20 mL of methanol, followed by 2 h of reflux performed under protection of argon. After part of the solvent was removed, the system was cooled for crystallization, giving 0.91 g of an asymmetric diimino ligand o-C₂₅H₂₅N₃, at a yield of 65%.

Application Example 7: Preparation of asymmetric tridentate ligand containing one alkylene group

With 30 mL of anhydrous alcohol used as the solvent and 1 mL of glacial acetic acid used as the catalyst, 1.2 mL of 3-amino-4-methylstyrene were reacted with 8.5 mmol of 2,6-diacetylpyridine under stirring at room temperature for 4 days. The solution was light yellow in color. After most of the solvent was removed, 40 mL of deionized water were added. A yellow precipitate appeared and was filtered. The precipitate was recrystallized using n-hexane to obtain a monoimino compound of columnar crystals. 4.0 mmol of the obtained monoimino compound, 10.0 mmol of 2,6-dimethylaniline, and 1 mL of glacial acetic acid were added to 25 mL of methanol, followed by 3 h of reflux performed under protection of argon. After part of the solvent was removed, the system was cooled for crystallization, giving 0.88 g of an asymmetric diimino ligand, o-C₂₆H₂₇N₃, at a yield of 58%.

Application Example 8: Preparation of asymmetric tridentate ligand containing one alkylene group

With 30 mL of anhydrous alcohol used as the solvent and 1 mL of glacial acetic acid used as the catalyst, 1.5 mL of 3-isopropyl-4-aminostyrene were reacted with 11.4 mmol of 2,6-diacetylpyridine under stirring at room temperature for 4 days. The solution was light yellow in color. After most of the solvent was removed, 40 mL of deionized water were added. A yellow precipitate appeared and was filtered. The precipitate was recrystallized using n-hexane to obtain a monoimino compound of columnar crystals. 5.0 mmol of the obtained monoimino compound, 10.9 mmol of 2,6-diisopropylaniline, and 2 mL of glacial acetic acid were added to 30 mL of methanol, followed by 2.5 h of reflux performed under protection of argon. After part of the solvent was removed, the system was cooled for crystallization, giving 1.23 g of an asymmetric diimino ligand, o-C₃₂H₃₉N₃, at a yield of 53%.

Application Example 9: Preparation of symmetric tridentate ligand containing two alkylene groups

With 20 mL of methanol used as the solvent, 1 mL of glacial acetic acid, 0.94 mL of o-aminostyrene, and 3.05 mmol of 2,6-diacetylpyridine were heated to slightly boiling under protection of argon, followed by 4 h of reflux and concentration in vacuo. Then, the reaction product was added to 30 mL of deionized water and extracted using ethyl ether. The extract was dried with anhydrous sodium sulfate and concentrated. The system was cooled for crystallization to obtain 0.95 g of a yellow crystal of a diimino ligand, o,o-C₂₅H₂₃N₃, at a yield of 85%.

Application Example 10: Preparation of symmetric tridentate ligand containing two alkylene groups

With 20 mL of methanol used as the solvent, 2 mL of glacial acetic acid, 1.2 mL of m-aminostyrene, and 3.92 mmol of 2,6-diacetylpyridine were added at the same time. The process was carried out in the same way as described in Application Example 9, giving 1.17 g of a diimino ligand, m,m-C₂₅H₂₃N₃, at a yield of 82%.

Application Example 11: Preparation of symmetric tridentate ligand containing two alkylene groups

With 30 mL of methanol used as the solvent, 2 mL of glacial acetic acid, 1.5 mL of p-aminostyrene, and 4.9 mmol of 2,6-diacetylpyridine were added at the same time. The process was carried out in the same way as described in Application Example 9, giving 1.43 g of a diimino ligand, p,p-C₂₅H₂₃N₃, at a yield of 80%.

Application Example 12: Preparation of late transition metal compound containing one alkylene group

Under oxygen-free and anhydrous conditions and under the protection of highly pure argon, 1.51 mmol of the ligand $o\text{-C}_{25}\text{H}_{25}\text{N}_3$ obtained in Application Example 6 were added to 30 mL of tetrahydrofuran, followed by adding 1.44 mmol of iron dichloride tetrahydrate. The system was stirred at room temperature for 1.5 h, followed by concentration in vacuo. n-hexane was added to precipitate a solid powder, which was washed 3 times with n-hexane, followed by drying in vacuo, giving 0.682 g of $o\text{-C}_{25}\text{H}_{25}\text{N}_3\text{Fe}$ at a yield of 96%.

Application Example 13: Preparation of late transition metal compound containing one alkylene group

Under oxygen-free and anhydrous conditions and under the protection of highly pure argon, 1.51 mmol of the ligand $o\text{-C}_{26}\text{H}_{27}\text{N}_3$ obtained in Application Example 7 was added to 35 mL of tetrahydrofuran, followed by adding 1.44 mmol of iron dichloride tetrahydrate. The system was stirred at room temperature for 2 h, followed by concentration in vacuo. n-hexane was added to precipitate a solid powder, which was washed 3 times with n-hexane, followed by drying in vacuo, giving 0.695 g of $o\text{-C}_{26}\text{H}_{27}\text{N}_3\text{Fe}$ at a yield of 95%.

Application Example 14: Preparation of late transition metal compound containing one alkylene group

Under oxygen-free and anhydrous conditions and under the protection of highly pure argon, 1.51 mmol of the ligand $o\text{-C}_{32}\text{H}_{39}\text{N}_3$ obtained in Application Example 8 was added to 30 mL of tetrahydrofuran, followed by adding 1.44 mmol of anhydrous cobalt dichloride. The system was stirred at room temperature for 1.5 h, followed by concentration in vacuo. n-hexane was added to precipitate a solid powder, which was washed 5 times with n-hexane, followed by drying in vacuo, giving 0.788 g of $o\text{-C}_{32}\text{H}_{39}\text{N}_3\text{Co}$ at a yield of 92%.

Application Example 15: Preparation of late transition metal compound containing one alkylene group

Under oxygen-free and anhydrous conditions and under the protection of highly pure argon, 1.51 mmol of the ligand $o,o\text{-C}_{25}\text{H}_{23}\text{N}_3$ obtained in Application Example 9 was added to 30 mL of tetrahydrofuran, followed by adding 1.37 mmol of iron dichloride tetrahydrate. The system was stirred at room temperature for 1.5 h, followed by concentration in vacuo. n-hexane was added to precipitate a solid powder, which was washed 4 times with n-hexane, followed by drying in vacuo, giving 0.64 g of $o,o\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe}$ at a yield of 95%.

Application Example 16: Preparation of late transition metal compound containing one alkylene group

Under oxygen-free and anhydrous conditions and under protection of highly pure argon, 1.51 mmol of the ligand m,m-C₂₅H₂₃N₃ obtained in Application Example 10 was added to 30 mL of tetrahydrofuran, followed by adding 1.37 mmol of iron dichloride tetrahydrate. The system was stirred at room temperature for 1 h, followed by concentration in vacuo. n-hexane was added to precipitate a solid powder, which was washed 5 times with n-hexane, followed by drying in vacuo, giving 0.647 g of m,m-C₂₅H₂₃N₃Fe at a yield of 96%.

Application Example 17: Preparation of late transition metal compound containing one alkylene group

Under oxygen-free and anhydrous conditions and under protection of highly pure argon, 1.51 mmol of the ligand p,p-C₃₂H₂₃N₃ obtained in Application Example 11 was added to 30 mL of tetrahydrofuran, followed by adding 1.37 mmol of anhydrous cobalt dichloride. The system was stirred at room temperature for 2 h, followed by concentration in vacuo. n-hexane was added to precipitate a solid powder, which was washed 3 times with n-hexane, followed by drying in vacuo, giving 0.664 g of o-C₂₅H₂₃N₃Co at a yield of 98%.

Application Example 18: Preparation of catalyst component A

Under anhydrous conditions, 2.0 mmol of the alkylene-containing catalyst o-C₂₅H₂₅N₃Fe obtained in Application Example 12 was added to 20 mL boiling dimethylamide, followed by adding 5 mL of styrene and 0.05 g of azodiisobutyronitrile. The reaction was carried out in an 80°C water bath for 12 h. Then, the dimethylamide was removed as much as possible under heating to obtain a gel-like substance, which was dissolved using 30 mL of toluene, followed by centrifugation. The supernatant was treated with n-hexane to obtain a solid powder, which was washed with n-hexane three times, giving catalyst component A p[S-co-(o-C₂₅H₂₅N₃Fe)]. The measured Fe content was 0.6 wt%.

Application Example 19: Preparation of catalyst component A

Under anhydrous conditions, 5.0 mmol of the alkylene containing catalyst o,o-C₂₅H₂₃N₃Fe obtained in Application Example 15 was added to 20 mL boiling dimethylamide, followed by adding 8 mL of styrene and 0.1 g of azodiisobutyronitrile. The reaction was carried out in an 80°C water bath for 14 h. Then, the dimethylamide was removed as much as possible under heating to obtain a gel-like substance, which was dissolved using 30 mL of toluene, followed by centrifugation. The supernatant was treated with n-hexane to

obtain a solid powder, which was washed with n-hexane three times, giving catalyst component A p[S-co-(o,o-C₂₅H₂₃N₃Fe)]. The measured Fe content was 1.46 wt%.

Application Example 20: Preparation of catalyst component A

Under anhydrous conditions, 10 mmol of the alkylene containing catalyst m,m-C₂₅H₂₃N₃Fe obtained in Application Example 16 was added to 20 mol boiling dimethylamide, followed by adding 10 mL of styrene and 0.14 g of azodiisobutyronitrile. The reaction was carried out in an 80°C water bath for 15 h. Then, the dimethylamide was removed as much as possible under heating to obtain a gel-like substance, which was dissolved using 30 mL of toluene, followed by centrifugation. The supernatant was treated with n-hexane to obtain a solid powder, which was washed with n-hexane three times, giving catalyst component A p[S-co-(m,m-C₂₅H₂₃N₃Fe)]. The measured Fe content was 0.7 wt%.

Application Example 21: Preparation of catalyst component A

Under anhydrous conditions, 10 mmol of the alkylene containing catalyst p,p-C₂₅H₂₃N₃Co obtained in Application Example 17 was added to 20 mol boiling dimethylamide, followed by adding 10 mL of styrene and 0.14 g of azodiisobutyronitrile. The reaction was carried out in an 80°C water bath for 15 h. Then, the dimethylamide was removed as much as possible under heating to obtain a gel-like substance, which was dissolved using 30 mL of toluene, followed by centrifugation. The supernatant was treated with n-hexane to obtain a solid powder, which was washed with n-hexane three times, giving catalyst component A p[S-co-(p,p-C₂₅H₂₃N₃Co)]. The measured Co content was 0.4 wt%.

Application Example 22: Ethylene polymerization

Under oxygen-free and anhydrous conditions, 100 mL of toluene were added to a 200-mL glass reaction bottle, and ethylene gas was fed into the bottle under normal pressure. 3 mL of a toluene solution containing 1M methylaluminoxane and 0.0187 g of the toluene solution of the catalyst component A p[S-co-(o-C₂₅H₂₅N₃Fe)] prepared in Application Example 18 were added sequentially under stirring, followed by 1 h of reaction carried out at 25°C. An alcohol solution containing 1% hydrochloric acid was used to end the reaction. The obtained polymer was filtered and washed with alcohol three times, followed by drying in vacuo at 40°C for 24 h, giving 1.8 g of polymer. The catalytic efficiency was 9.0×10^5 g PE/molFe·h.

Application Example 23: Ethylene polymerization

Under oxygen-free and anhydrous conditions, 100 mL of hexane were added to a 200-mL glass reaction bottle, and ethylene gas was fed into the bottle under normal pressure. 1 mL of a

toluene solution containing 1M methylaluminoxane and 0.028 g of the toluene suspension of the catalyst component A p[S-co-(p,p-C₂₅H₂₃N₃Co)] prepared in Application Example 21 were added sequentially under stirring, followed by 1 h of reaction carried out at 40°C. An alcohol solution containing 1% hydrochloric acid was used to end the reaction. The obtained polymer was filtered and washed with alcohol three times, followed by drying in vacuo at 40°C for 24 h, giving 0.8 g of polymer. The catalytic efficiency was 4.0×10^5 g PE/molFe·h.

Application Example 24: Ethylene polymerization

Under oxygen-free and anhydrous conditions, 100 mL of toluene were added to a 200-mL glass reaction bottle, and ethylene gas was fed into the bottle under normal pressure. 5 mL of a toluene solution containing 1M methylaluminoxane and 0.028 g of the toluene suspension of the catalyst component A p[S-co-(p,p-C₂₅H₂₃N₃Co)] prepared in Application Example 21 were added sequentially under stirring, followed by 1 h of reaction carried out at 50°C. An alcohol solution containing 1% hydrochloric acid was used to end the reaction. The obtained polymer was filtered and washed with alcohol three times, followed by drying in vacuo at 40°C for 24 h, giving 1.2 g of polymer. The catalytic efficiency was 6.0×10^5 g PE/molFe·h.

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[54] 发明名称 高分子化“茂后”烯烃聚合催化剂的制备方法

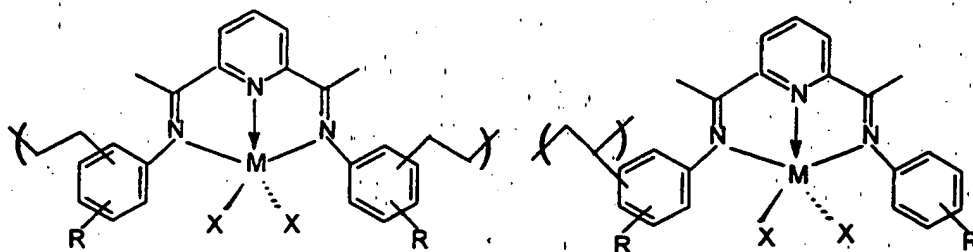
[57] 摘要

本发明是属于高分子化后过渡金属“茂后”烯烃聚合催化剂的制备,催化剂由 A 和 B 两组分组成,A 组分表达式为 $[P(S-co-Cat)]$,P 表示共聚物,S 为聚苯乙烯,co 表示共聚,Cat 表示“茂后”催化剂。Cat 是由三齿氮中性配体与金属 M 所形成的配位化合物,B 组份为甲基铝氧烷或五氟苯硼。这两类催化剂催化乙烯聚合催化活性高,聚合产物不含无机灰分。

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权 利 要 求 书

1. 一种高分子化“茂后”烯烃聚合催化剂的制备方法，其特征在于催化剂由 A 和 B 两组分组成，A 组分表达式为 $[P(S-co-Cat)]$ ，P 表示共聚物，S 为聚苯乙烯，co 表示共聚，Cat 表示“茂后”催化剂，具体结构如下：

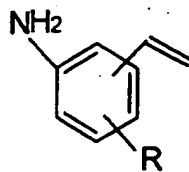


其中 $M = Fe, Co$; $X = Cl, Br$; R 为 H、Me、i-Pr、t-Bu 其中的任意一种，Cat 是由三齿氮中性配体与金属 M 所形成的配位化合物，B 组份为甲基铝氧烷或五氟苯硼；

催化剂的制备过程如下：

1)、烯烷基芳胺的制备

其结构为：



在无氧无水的条件下，以干燥的四氢呋喃 50-70ml 为溶剂，冰水冷却，加入 51mmol-74mmol 甲基三苯基溴化磷与 51mmol-78mmol 正丁基锂进行反应，30-60 分钟后，加入硝基芳甲醛 50mmol-74mmol，反应 12-18 小时，所得混合液经盐水洗涤，三氯甲烷萃取，无水硫酸钠干燥后真空浓缩，残留液通过硅胶柱分离，淋洗剂为甲苯/己烷 1:1，得硝基芳乙烯，产率 72-89%，再经过铁-醋酸-乙醇体系还原制得烯烷基芳胺，产率 56-60%；

2)、含有两个烯烃基团的对称型三齿配体的制备

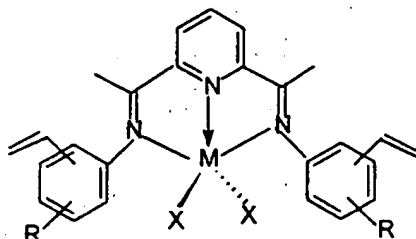
以 20-30ml 甲醇为溶剂, 同时加入 1-2ml 冰醋酸, 0.94-1.5ml 烯烃基芳胺, 与 3.05-4.9mmol 2,6-二乙酰基吡啶, 氩气保护下加热至微沸回流 4 小时, 真空浓缩, 倾入 30ml 的去离子水中, 用乙醚萃取, 无水硫酸钠干燥, 浓缩, 冷却结晶得黄色二亚胺配体的结晶, 产率 80-85%;

3)、含有单个烯烃基团的不对称型三齿配体的制备

以 20-30ml 无水乙醇为溶剂, 冰醋酸 0.5-1ml 为催化剂, 0.8-1.5ml 烯烃基芳胺与 6.1-11.4mmol 2,6-二乙酰基吡啶在室温下搅拌反应 3-4 天, 溶液呈亮黄色, 抽去溶剂, 加入 30-40ml 去离子水, 出现黄色沉淀, 过滤, 沉淀用正己烷重结晶, 得单亚胺化合物, 取 3.8-5.0mmol 该单亚胺化合物, 8.3-10.9mmol 芳胺, 1-2ml 冰醋酸加入到 20-30ml 甲醇中, 氩气保护下回流 2-3 小时, 抽去溶剂, 冷却结晶, 得不对称型的二亚胺配体, 产率 53-65%;

4)、对称型含有两个烯烃基团的后过渡金属催化剂的制备

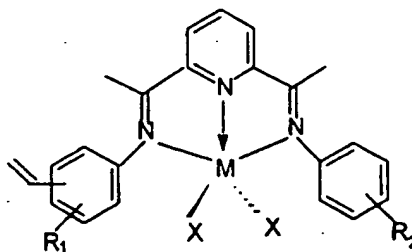
其结构式为:



催化剂的制备在无氧无水及高纯氩气保护条件下进行, 以 30-40ml 四氢呋喃为溶剂, 对称型二亚胺配体与四水合二氯化铁或无水二氯化钴按 1.1:1 投料, 室温搅拌 1-2 小时, 真空浓缩, 加正己烷沉淀出固体粉末, 并用正己烷洗涤 3-5 次, 真空干燥, 产率 95-98%;

5)、不对称型含单个烯烃基团的后过渡金属催化剂的制备

其结构式为:



催化剂的制备在无氧无水及高纯氩气保护条件下进行, 以

30-40ml 四氢呋喃为溶剂，不对称型配体与四水合二氯化铁或无水二氯化钴按 1.05:1 投料，室温搅拌 1.5-3 小时，真空浓缩，加正己烷沉淀出固体粉末，并用正己烷洗涤 3-5 次，真空干燥，产率 92-96%；

6)、高分子化“茂后”催化剂的制备

在无氧无水条件下，将含有烯烃基团的“茂后”催化剂 2-10mmol，苯乙烯 5-10ml，偶氮二异丁腈 0.05-0.14g，依次加入到蒸过的二甲基酰胺中混合均匀，然后在 80℃ 的水浴中共聚 12-15 小时，在加热条件下，抽去二甲基甲酰胺，得到胶状物，用甲苯 30ml 溶解，离心，清液用正己烷作沉淀剂，得固体粉末，再用正己烷洗涤三次，烘干；乙烯聚合在无水无氧条件下进行，在反应体系中依次加入甲苯或己烷 100ml、甲基铝氧烷、高分子化催化剂 Al/M=500-2500、乙烯，于 25-50℃ 反应 1 小时，用含 1% 盐酸的乙醇溶液终止反应，将所得产物过滤，用乙醇洗涤 3 次，并于 40℃ 真空干燥 24 小时。

2. 如权利要求 1 所述的高分子化“茂后”烯烃聚合催化剂的制备方法，其特征在于，对称型二亚胺配体与四水合二氯化铁按 1.1:1 投料。

3. 如权利要求 1 所述的高分子化“茂后”烯烃聚合催化剂的制备方法，其特征在于，对称型二亚胺配体与无水二氯化钴按 1.1:1 投料。

4. 如权利要求 1 所述的高分子化“茂后”烯烃聚合催化剂的制备方法，其特征在于，不对称型二亚胺配体与四水合二氯化铁按 1.05:1 投料。

5. 如权利要求 1 所述的高分子化“茂后”烯烃聚合催化剂的制备方法，其特征在于，不对称型二亚胺配体与无水二氯化钴按 1.05:1 投料。

6. 如权利要求 1 所述的高分子化“茂后”烯烃聚合催化剂的制备方法，其特征在于，所述乙烯聚合在无水无氧条件下进行，在反应体系中加入甲苯 100ml。

7. 如权利要求 1 所述的高分子化“茂后”烯烃聚合催化剂的制备方法，其特征在于，所述乙烯聚合在无水无氧条件下进行，在反应体系中加入己烷 100ml。

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8. 如权利要求 1 所述的高分子化“茂后” 烯烃聚合催化剂的制备方法，其特征在于，所述乙烯聚合在无水无氧条件下进行，在反应体系中加入甲基铝氧烷、高分子化催化剂 $Al/M=500-2500$ 。

9. 如权利要求 1 所述的高分子化“茂后” 烯烃聚合催化剂的制备方法，其特征在于，所述乙烯聚合在无水无氧条件下进行，在反应体系中加入乙烯。

说明书

高分子化“茂后”烯烃聚合催化剂的制备方法

本发明属于高分子化“茂后”后过渡金属烯烃聚合催化剂的制备方法。

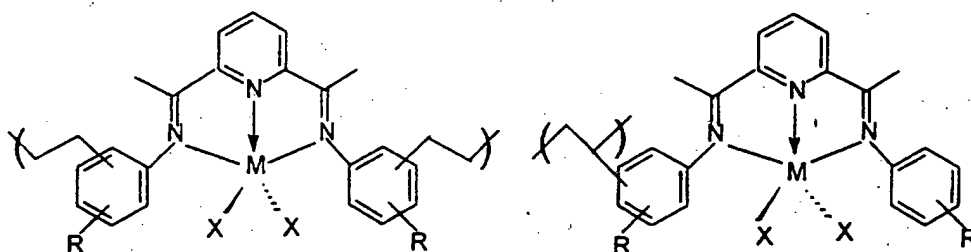
聚烯烃是现代高分子材料工业的支柱产业之一，全球每年生产千万吨聚烯烃产品，这些产品改善了人类的生存环境和生活条件。烯烃在催化剂的作用下，形成聚合物，变化催化剂的结构可以得到特定结构、特定性能的聚烯烃产物，所以催化剂是聚烯烃产业的核心。最近几年，人们在茂金属催化剂的基础上发现了一系列新型单活性中心烯烃聚合催化剂，这系列催化剂大致可以分为两类：a. 非茂体系化合物以及含有环戊二烯基的非 IVB 族过渡金属化合物；b. 后过渡金属镍、钯、铁、钴等多亚胺类化合物。因为这系列催化剂是在茂金属催化剂之后发现的，所以人们把它们统称为“茂后”烯烃聚合催化剂。

一九九八年，Brookhart 等人以及 Du Pont 公司(*J. Am. Chem. Soc.* 120. 4049(1998), WO98/30612, WO98/27124.)和 Gibson 等人以及 BP 公司(*Chem. commun.* 849. 1998, WO99/12981)分别报道了铁、钴的多亚胺类化合物在助催化剂 MMAO 存在下具有催化烯烃聚合的能力，而且活性极高。这一发现为“茂后”烯烃聚合催化剂的研究开拓了一个新的领域。这种铁、钴的多亚胺类化合物催化乙烯聚合生成线型高密度聚乙烯，聚合物分子量则容易受取代基、中心金属原子及活性点浓度的影响。Brookhart 小组和 Gibson 小组分别详细研究了芳胺中 2、4、6 位上取代基团对于催化剂结构及催化性能的影响。取代基团包括甲基、异丙基和叔丁基。研究表明，特别是 2、6 位取代基团越大，越有利于产生高分子量的聚乙烯。后过渡金属“茂后”催化剂的固载化的工作至今还未见报道，为了使这类催化剂能够适应工业化装置，固载化的工作具有一定的意义。

本发明的目的是提供一种高分子化的“茂后”烯烃聚合催化剂的制备方法。该方法采用含烯烃取代基团的铁、钴多胺类化合物与苯乙烯在引发剂作用下，将“茂后”催化剂通过 σ 键连接到高分子链上形成高分子化的“茂后”烯烃聚合催化剂。

高分子化的“茂后”催化剂对烯烃聚合同样具有很高的催化活性，而且将“茂后”催化剂高分子化可以很容易地控制催化剂在分子链上的组成、分布，通过调节催化剂在分子链上的分布可以最大限度地发挥活性中心的催化作用，另外高分子化“茂后”催化剂催化烯烃聚合所得到的聚合物不含无机灰分。

本发明制备的催化剂由 A 和 B 两组分组成，A 组分表达式为 $[P(S-co-Cat)]$ ，P 表示共聚物，S 为聚苯乙烯，co 表示共聚，Cat 表示“茂后”催化剂。具体结构如下：



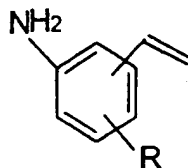
其中 $M = Fe, Co$; $X = Cl, Br$; R 为 H、Me、i-Pr、t-Bu 其中的任意一种

Cat 是由三齿氮中性配体与金属 M 所形成的配位化合物，其中胺的邻、间、对位上含有烯基团通过与苯乙烯共聚使得催化剂通过 σ 键与高分子链联结，得到高分子化“茂后”烯烃聚合催化剂。B 组份为甲基铝氧烷或五氟苯硼。

催化剂的制备过程如下：

1)、烯基芳胺的制备

其结构为：



在无氧无水的条件下，以干燥的四氢呋喃 50-70ml 为溶剂，冰水冷却，加入 51mmol-74mmol 甲基三苯基溴化磷与 51mmol-78mmol 正丁基锂进行反应，30-60 分钟后，加入硝基芳甲醛 50mmol-74mmol，反应 12-18 小时，所得混合液经盐水洗涤，三氯甲烷萃取，无水硫酸钠干燥后真空浓缩，残留液通过硅胶柱分

离，淋洗剂为甲苯/己烷 1:1，得硝基芳乙烯，产率 72—89%，再经过铁—醋酸—乙醇体系还原制得烯烃基芳胺，产率 56—60%

2)、含有两个烯烃基团的对称型三齿配体的制备

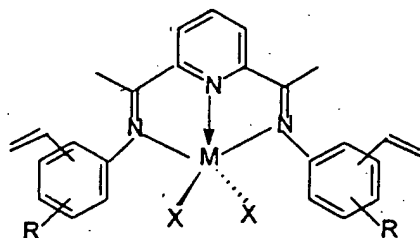
以 20-30ml 甲醇为溶剂，同时加入 1-2ml 冰醋酸，0.94-1.5ml 烯烃基芳胺，与 3.05-4.9mmol 2,6-二乙酰基吡啶，氩气保护下加热至微沸回流 4 小时，真空浓缩，倾入 30ml 的去离子水中，用乙醚萃取，无水硫酸钠干燥，浓缩，冷却结晶得黄色二亚胺配体的结晶，产率 80—85%。

3)、含有单个烯烃基团的不对称型三齿配体的制备

以 20-30ml 无水乙醇为溶剂，冰醋酸 0.5-1ml 为催化剂，0.8-1.5ml 烯烃基芳胺与 6.1-11.4mmol 2,6-二乙酰基吡啶在室温下搅拌反应 3-4 天，溶液呈亮黄色，抽去大部分溶剂，加入 30-40ml 去离子水，出现黄色沉淀，过滤，沉淀用正己烷重结晶，得单亚胺化合物。取 3.8-5.0mmol 该单亚胺化合物，8.3-10.9mmol 芳胺，1-2ml 冰醋酸加入到 20-30ml 甲醇中，氩气保护下回流 2-3 小时，抽去部分溶剂，冷却结晶，得不对称型的二亚胺配体，产率 53-65%。

4)、对称型含有两个烯烃基团的后过渡金属催化剂的制备

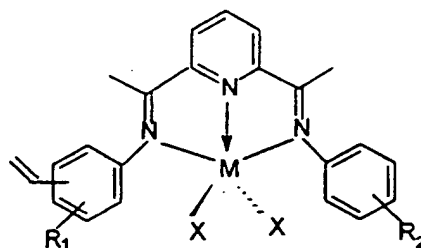
其结构式为：



催化剂的制备在无氧无水及高纯氩气保护条件下进行。以 30-40ml 四氢呋喃为溶剂，对称型二亚胺配体与四水合二氯化铁或无水二氯化钴按 1.1:1 投料，室温搅拌 1-2 小时，真空浓缩，加正己烷沉淀出固体粉末，并用正己烷洗涤 3-5 次，真空干燥，产率 95—98%。

5)、不对称型含单个烯烃基团的后过渡金属催化剂的制备

其结构式为：



催化剂的制备在无氧无水及高纯氩气保护条件下进行。以 30-40ml 四氢呋喃为溶剂，不对称型配体与四水合二氯化铁或无水二氯化钴按 1.05: 1 投料，室温搅拌 1.5-3 小时，真空浓缩，加正己烷沉淀出固体粉末，并用正己烷洗涤 3-5 次，真空干燥，产率 92-96%。

6)、高分子化“茂后”催化剂的制备

在无氧无水条件下，将含有烯烷基团的“茂后”催化剂 2-10mmol，苯乙烯 5-10ml，偶氮二异丁腈 0.05-0.14g，依次加入到蒸过的二甲基酰胺中混合均匀，然后在 80℃ 的水浴中共聚 12-15 小时。在加热条件下尽量抽去二甲基甲酰胺，得到胶状物，用甲苯 30ml 溶解，离心，清液用正己烷作沉淀剂，得固体粉末，再用正己烷洗涤三次，烘干即可。

乙烯聚合在无氧无水条件下进行，在反应体系中依此加入甲苯或己烷 100ml、甲基铝氧烷、高分子化催化剂 Al/M=500-2500、乙烯于 25-50℃ 反应 1 小时，用含 1% 盐酸的乙醇溶液终止反应，将所得产物过滤，用乙醇洗涤 3 次，并于 40℃ 真空干燥 24 小时。

本发明提供的实施例如下：

实施例 1: 烯烷基芳胺的制备

氩气氛下 51mmol 甲基三苯基溴化磷溶解于 50ml 干燥的四氢呋喃中，冰水冷却，依次加入 32ml 1.6M 的正丁基锂，30 分钟后向其中加入 100ml 溶有 50mmol 的邻硝基苯甲醛的四氢呋喃溶液，反应 12 小时，盐水洗涤，三氯甲烷萃取，萃取液用无水硫酸钠干燥，真空浓缩，残留液通过硅胶柱分离，淋洗剂为甲苯/己烷 1:1，得黄色液体—邻硝基苯乙烯 6.63g，产率 89.0%。将所得邻硝基苯乙烯 45mmol 溶于 50ml 冰醋酸和 50ml 无水乙醇的混合溶液中加入铁粉 0.178mol，混合溶液在氩气保护下回流 1 小时，冷却至室温，倾入 350ml 水中，用固体碳酸钠中和至中性，稠溶液用乙醚萃取，真空浓缩，残留液中加入少量对苯二酚减压蒸馏，得无色液体—邻氨基苯乙烯 3.2g，产率 60.0%。

实施例 2: 烯烷基芳胺的制备

操作同实施例 1，其中间硝基苯甲醛的用量为 50mmol，制得间氨基苯乙烯 2.17g，产率 41.5%。

实施例 3: 烯烷基芳胺的制备

操作同实施例 1，其中对硝基苯甲醛的用量为 50mmol，制得对氨基苯乙烯 3.02g，产率 50.7%。

实施例 4: 烯炔基芳胺的制备

氩气氛下 74mmol 甲基三苯基溴化磷溶解于 70ml 干燥的四氢呋喃中，冰水冷却，依次加入 48.8ml 1.6M 的正丁基锂，50 分钟后向其中加入 100ml 溶有 74mmol 的 3-硝基 4-甲基苯甲醛的四氢呋喃溶液，搅拌反应 16 小时，盐水洗涤，三氯甲烷萃取，萃取液用无水硫酸钠干燥，真空浓缩，残留液通过硅胶柱分离，淋洗剂为甲苯/己烷 1:1，得黄色液体—3-硝基 4-甲基苯乙烯 8.68g，产率 72.0%。将所得邻硝基苯乙烯 45mmol 溶于 50ml 冰醋酸和 50ml 无水乙醇的混合溶液中加入铁粉 0.178mol，混合溶液在氩气保护下回流 1 小时，冷却至室温，倾入 350ml 水中，用固体碳酸钠中和至中性，稠溶液用乙醚萃取，真空浓缩，残留液中加入少量对苯二酚减压蒸馏，得无色液体—3-氨基 4-甲基苯乙烯 3.41g，产率 57%。

实施例 5: 烯炔基芳胺的制备

氩气氛下 60mmol 甲基三苯基溴化磷溶解于 60ml 干燥的四氢呋喃中，冰水冷却，依次加入 37.5ml 1.6M 正丁基锂，60 分钟后向其中加入 100ml 溶有 60mmol 的 3-异丙基 4-硝基苯甲醛的四氢呋喃溶液，搅拌反应 18 小时，盐水洗涤，三氯甲烷萃取，萃取液用无水硫酸钠干燥，真空浓缩，残留液通过硅胶柱分离，淋洗剂为甲苯/己烷 1:1，得黄色液体—3-异丙基 4-硝基苯乙烯 9.11g，产率 79.5%。将所得邻硝基苯乙烯 45mmol 溶于 50ml 冰醋酸和 50ml 无水乙醇的混合溶液中加入铁粉 0.178mol，混合溶液在氩气保护下回流 1 小时，冷却至室温，倾入 350ml 水中，用固体碳酸钠中和至中性，稠溶液用乙醚萃取，真空浓缩，残留液中加入少量对苯二酚减压蒸馏，得无色液体—3-异丙基 4-氨基苯乙烯 4.06g，产率 56.0%。

实施例 6: 含有单个烯炔基团的不对称型三齿配体的制备

以 20ml 无水乙醇为溶剂，0.5ml 冰醋酸为催化剂，0.8ml 邻氨基苯乙烯和 6.1mmol 2,6-二乙酰基吡啶在室温下搅拌反应 3 天，溶液呈亮黄色，抽去大部分溶剂，加入去离子水 30ml，出现黄色沉淀，过滤，沉淀用正己烷重结晶，得柱状晶体的单亚胺化合物。取 3.8mmol 该单亚胺化合物和 8.3mmol 2,6-二甲基苯胺，1ml 冰醋酸加入到 20ml

甲醇中，氩气保护下回流 2 小时，抽去部分溶剂，冷却结晶，得不对称型的二亚胺配体 $o\text{-C}_{25}\text{H}_{25}\text{N}_3$ 0.91g，产率 65%。

实施例 7: 含有单个烯烃基团的不对称型三齿配体的制备

以 30ml 无水乙醇为溶剂，1ml 冰醋酸为催化剂，1.2ml 3-氨基 4-甲基苯乙烯和 8.5mmol 2,6-二乙酰基吡啶在室温下搅拌反应 4 天，溶液呈亮黄色，抽去大部分溶剂，加入去离子水 40ml，出现黄色沉淀，过滤，沉淀用正己烷重结晶，得柱状晶体的单亚胺化合物。取 4.0mmol 该单亚胺化合物和 10.0mmol 2,6-二甲基苯胺，1ml 冰醋酸加入到 25ml 甲醇中，氩气保护下回流 3 小时，抽去部分溶剂，冷却结晶，得不对称型的二亚胺配体 $o\text{-C}_{26}\text{H}_{27}\text{N}_3$ 0.88g，产率 58%。

实施例 8: 含有单个烯烃基团的不对称型三齿配体的制备

以 30ml 无水乙醇为溶剂，1ml 冰醋酸为催化剂，1.5ml 3-异丙基 4-氨基苯乙烯和 11.4mmol 2,6-二乙酰基吡啶在室温下搅拌反应 4 天，溶液呈亮黄色，抽去大部分溶剂，加入去离子水 40ml，出现黄色沉淀，过滤，沉淀用正己烷重结晶，得柱状晶体的单亚胺化合物。取 5.0mmol 该单亚胺化合物和 10.9mmol 2,6-二异丙基基苯胺，2ml 冰醋酸加入到 30ml 甲醇中，氩气保护下回流 2.5 小时，抽去部分溶剂，冷却结晶，得不对称型的二亚胺配体 $o\text{-C}_{32}\text{H}_{39}\text{N}_3$ 1.23g，产率 53%。

实施例 9: 含有两个烯烃基团的对称型三齿配体的制备

以 20ml 甲醇为溶剂同时加入 1ml 冰醋酸，0.94ml 邻氨基苯乙烯，和 3.05mmol 2,6 二乙酰基吡啶，氩气氛下微沸回流 4 小时，真空浓缩，倾入 30ml 的去离子水中，用乙醚萃取，无水硫酸钠干燥，浓缩，冷却结晶得二亚胺配体 $o,o\text{-C}_{25}\text{H}_{23}\text{N}_3$ 0.95g，产率 85%。

实施例 10: 含有两个烯烃基团的对称型三齿配体的制备

以 20ml 甲醇为溶剂同时加入 2ml 冰醋酸，1.2ml 间氨基苯乙烯，和 3.92 mmol 2,6 二乙酰基吡啶，按实施例 9 操作，得二亚胺配体 $m,m\text{-C}_{25}\text{H}_{23}\text{N}_3$ 1.17g，产率 82%。

实施例 11: 含有两个烯烃基团的对称型三齿配体的制备

以 30ml 甲醇为溶剂同时加入 2ml 冰醋酸，1.5ml 对氨基苯乙烯，

和 4.9 mmol 2.6 二乙酰基吡啶, 按实施例 9 操作, 得二亚胺配体 $p,p\text{-C}_{25}\text{H}_{23}\text{N}_3$ 1.43g, 产率 80%。

实施例 12: 含单个烯烃基的后过渡金属化合物制备

在无氧无水及高纯氩气保护条件下, 取 1.51mmol 实施例 6 所制备的配体 $o\text{-C}_{25}\text{H}_{25}\text{N}_3$ 溶解于 30ml 四氢呋喃中, 加入 1.44mmol 四水合二氯化铁, 室温搅拌 1.5 小时, 真空浓缩, 加正己烷沉淀出固体粉末, 并用正己烷洗涤 3 次, 真空干燥, 即得 $o\text{-C}_{25}\text{H}_{25}\text{N}_3\text{Fe}$ 0.682g, 产率 96%。

实施例 13: 含单个烯烃基的后过渡金属化合物制备

在无氧无水及高纯氩气保护条件下, 取 1.51mmol 实施例 7 所制备的配体 $o\text{-C}_{26}\text{H}_{27}\text{N}_3$ 溶于 35ml 四氢呋喃中, 加入 1.44mmol 四水合二氯化铁, 室温搅拌 2 小时, 真空浓缩, 加正己烷沉淀出固体粉末, 并用正己烷洗涤 3 次, 真空干燥, 即得 $o\text{-C}_{26}\text{H}_{27}\text{N}_3\text{Fe}$ 0.695g, 产率 95%。

实施例 14: 含单个烯烃基的后过渡金属化合物制备

在无氧无水及高纯氩气保护条件下, 取 1.51mmol 实施例 8 所制备的配体 $o\text{-C}_{32}\text{H}_{39}\text{N}_3$ 溶于 30ml 四氢呋喃中, 加入 1.44mmol 无水二氯化钴, 室温搅拌 3 小时, 真空浓缩, 加正己烷沉淀出固体粉末, 并用正己烷洗涤 5 次, 真空干燥, 即得 $o\text{-C}_{32}\text{H}_{39}\text{N}_3\text{Co}$ 0.788g, 产率 92%。

实施例 15: 含两个烯烃基的后过渡金属化合物制备

在无氧无水及高纯氩气保护条件下, 取 1.51mmol 实施例 9 所制备的配体 $o,o\text{-C}_{25}\text{H}_{23}\text{N}_3$ 溶于 30ml 四氢呋喃中, 加入 1.37mmol 四水合二氯化铁, 室温搅拌 1.5 小时, 真空浓缩, 用正己烷沉淀出固体粉末, 并用正己烷洗涤 4 次, 真空干燥, 即得 $o,o\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe}$ 0.64g, 产率 95%。

实施例 16: 含两个烯烃基的后过渡金属化合物制备

在无氧无水及高纯氩气保护条件下, 取 1.51mmol 实施例 10 所制备的配体 $m,m\text{-C}_{25}\text{H}_{23}\text{N}_3$ 溶于 30ml 四氢呋喃中, 加入 1.37mmol 四水合二氯化铁, 室温搅拌 1 小时, 真空浓缩, 用正己烷沉淀出固体粉末, 并用正己烷洗涤 5 次, 真空干燥, 即得 $m,m\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe}$ 0.647g, 产率 96%。

实施例 17: 含两个烯烃基的后过渡金属化合物制备

在无氧无水及高纯氩气保护条件下, 取 1.51mmol 实施例 11 所制备的配体 $p,p\text{-C}_{25}\text{H}_{23}\text{N}_3$ 溶于 30ml 四氢呋喃中, 加入 1.37mmol 无水二氯化钴, 室温搅拌 2 小时, 真空浓缩, 用正己烷沉淀出固体粉末, 并用正己烷洗涤 3 次, 真空干燥, 即得 $p,p\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Co}$ 0.664g, 产率 98%.

实施例 18: 催化剂 A 组分的制备

在无氧无水条件下, 取 2.0mmol 实施例 12 制得含烯烃基团的催化剂 $o\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe}$, 加入到 20ml 的蒸过的二甲基甲酰胺中, 并加入 5ml 苯乙烯和 0.05g 偶氮二异丁腈, 将反应液置于 80℃ 恒温水浴中反应 12 小时, 在加热条件下尽量抽去二甲基甲酰胺, 得胶状物, 用 30ml 甲苯溶解固体, 离心, 清液用正己烷沉淀, 得固体粉末, 再用正己烷洗涤 3 次, 即得催化剂 A 组份 $p[\text{S-co}(o\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe})]$, 测定 Fe 含量为 0.6wt%.

实施例 19: 催化剂 A 组分的制备

在无氧无水条件下, 取 5.0mmol 实施例 15 制得含烯烃基团的催化剂 $o,o\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe}$ 加入到 20 ml 蒸过的二甲基甲酰胺中, 加入 8ml 苯乙烯和 0.1g 偶氮二异丁腈, 将反应液置于 80℃ 恒温水浴中反应 14 小时, 在加热条件下尽量抽去二甲基甲酰胺, 得胶状物, 用 30ml 甲苯溶解固体, 离心, 清液用正己烷沉淀, 得固体粉末, 再用正己烷洗涤 3 次, 即得催化剂 A 组份 $p[\text{S-co}(o,o\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe})]$, 测定 Fe 含量为 1.46wt%.

实施例 20: 催化剂 A 组分的制备

在无氧无水条件下, 取 10mmol 实施例 16 制得含烯烃基团的催化剂 $m,m\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe}$ 加入到 20ml 蒸过的二甲基甲酰胺中, 加入 10ml 苯乙烯和 0.14g 偶氮二异丁腈, 将反应液置于 80℃ 恒温水浴中反应 15 小时, 在加热条件下尽量抽去二甲基甲酰胺, 得胶状物, 用 30ml 甲苯溶解固体, 离心, 清液用正己烷沉淀, 得固体粉末, 再用正己烷洗涤 3 次, 即得催化剂 A 组份 $p[\text{S-co}(m,m\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe})]$, 测定铁含量为 0.7wt%.

实施例 21: 催化剂 A 组分的制备

在无氧无水条件下, 取 10mmol 实施例 17 制得含烯烃基团的催化剂 $p,p\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Co}$ 加入到 20ml 蒸过的二甲基甲酰胺中, 加入 10ml 苯乙烯和 0.14g 偶氮二异丁腈, 将反应液置于 80℃ 恒温水浴中

反应 15 小时，在加热条件下尽量抽去二甲基甲酰胺，得胶状物，用 30ml 甲苯溶解固体，离心，清液用正己烷沉淀，得固体粉末，再用正己烷洗涤 3 次，即得催化剂 A 组份 $p[S-co-(p,p-C_{25}H_{23}N_3Co)]$ ，测定铁含量为 0.4wt%。

实施例 22: 乙烯聚合

无氧无水条件下，在 200ml 玻璃反应瓶中加入 100ml 甲苯，常压通入乙烯气体，在搅拌下依次加入 3ml 浓度为 1M 的甲基铝氧烷的甲苯溶液和 0.0187g 的实施例 18 所制备的催化剂 A 组分 $p[S-co-(o-C_{25}H_{23}N_3Fe)]$ 的甲苯溶液，聚合反应于 25℃ 下聚合 1 小时，用含 1% 盐酸的乙醇溶液终止反应，将所得聚合物过滤，乙醇洗涤 3 次，并于 40℃ 真空干燥 24 小时，得聚合物 1.8g，催化效率为 $9.0 \times 10^5 g PE/molFe \cdot 小时$ 。

实施例 23: 乙烯聚合

无氧无水条件下，在 200ml 玻璃反应瓶中，加入 100ml 己烷，常压通入乙烯气体，在搅拌下依次加入 1ml 浓度为 1M 的甲基铝氧烷的甲苯溶液和含 0.028g 的实施例 21 所制备的催化剂 A 组分 $p[S-co-(p,p-C_{25}H_{23}N_3Co)]$ 的甲苯悬浮液，聚合反应于 40℃ 下聚合 1 小时，用含 1% 盐酸的乙醇溶液终止反应，将所得聚合物过滤，乙醇洗涤 3 次，并于 40℃ 真空干燥 24 小时，得聚合物 0.8g，催化效率为 $4.0 \times 10^5 g PE/molFe \cdot hr$ 。

实施例 24: 乙烯聚合

无氧无水条件下，在 200ml 玻璃反应瓶中，加入 100ml 甲苯，常压通入乙烯气体，在搅拌下依次加入 5ml 浓度为 1M 的甲基铝氧烷的甲苯溶液和含 0.028g 的实施例 21 所制备的催化剂 A 组分 $p[S-co-(p,p-C_{25}H_{23}N_3Co)]$ 的甲苯悬浮液，聚合反应于 50℃ 下聚合 1 小时，用含 1% 盐酸的乙醇溶液终止反应，将所得聚合物过滤，乙醇洗涤 3 次，并于 40℃ 真空干燥 24 小时，得聚合物 1.2g，催化效率为 $6.0 \times 10^5 g PE/molFe \cdot hr$ 。